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July 1, 1952

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ABSTRACT

Methods are described for electroplating nickel on zirconium and zirconium-tin alloys with as-plated adhesion > 6, 000 psi, and heat treating to produce alloy-diffusion bonds of 50, 000 psi. This supplements the results previously reported (BMI-707). Other metals can be electroplated over nickel, diffusion bonded to the zirconium or zirconium alloy.

A method of preparing zirconium for tin, lead-tin-solder, and silver-solder coating is also described. Other metals can be electrodeposited on these coatings.

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INTRODUCTION

In a previous report(1), a method for applying adherent electroplated metals to zirconium was described. The method depends on four prescribed operations to produce excellent bonds between the electroplated metal and the zirconium: etching, electroplating, prebaking, and heat treating.

The investigation was continued to study the process further with the following objectives:

A. To diffusion bond electroplated nickel to zirconium-tin alloys.

B. To find a method or methods for electroplating on zirconium or zirconium alloys so as to provide as-plated adhesion (>40,000 psi) and avoid heat treatment.

SUMMARY OF RESULTS AND CONCLUSIONS

For Diffusion Bonding

The procedure for diffusion bonding nickel to zirconium was investigated further and minor changes were incorporated providing an improved process. The improved process produces excellent diffusion bonds (50,000 psi) of nickel to Bureau of Mines zirconium, crystal-bar zirconium, and zirconium-tin alloy (crystal-bar zirconium with 2.5 per cent tin).

The following procedure is recommended for diffusion alloy bonding of electroplated nickel to zirconium or zirconium alloy:

I Starting Material

A. Zirconium or zirconium alloy

1. Arc-melted, fabricated sheet

(1) W. C. Schickner, J. G. Beach, C. L. Faust, "Electroplating on Zirconium", BMI-707, November 15, 1951.

a. Bureau of Mines (magnesium reduced)
b. Crystal bar (iodide, De Boer)
c. Zirconium-tin alloy (2.5 per cent tin-crystal-bar zirconium)

B. Surface finish

1. Preferred

a. Surface ground
b. Chemically polished (4 per cent HF solution)

2. Second choice

a. Vapor blasted
b. Sandblasted

II Alkaline Cleaning

A. Note: Electrolytic or soak alkaline cleaning in a proprietary alkaline cleaner (Anodex[2] was used)

III Rinse

IV Zirconium Etch

A. Solution specifications

1. Composition

NH_4F,	18 to 52 g/l or 0.5 to 1.4 molar
HF,	3 to 16 g/l or 0.15 to 0.8 molar
NH_4F/HF, molar	ratio of 1.2 to 4.1

2. Temperature, 100 F

B. Container, polyethylene

C. Metal removal

1. Bureau of Mines zirconium

Amount removed is not critical.

(2) Marketed by MacDermid Corporation, Waterbury, Connecticut.

2. Crystal-bar zirconium and zirconium-tin alloy

   Amount removed is 0.2 to 0.6 mil; about 0.6 mil removed in 3/4 minute for a solution containing 36 g/l NH_4F and 15.5 g/l HF, and 3 minutes for a solution containing 52 g/l NH_4F and 7 g/l HF.

V Rinse

VI Nickel Electroplate

A. Solution specifications

1. Composition (Watts bath, without wetting agent, low pH)

$NiSO_4 \cdot 7H_2O$,	330 g/l
$NiCl_2 \cdot 6H_2O$,	46 g/l
H_3BO_3,	37 g/l
H_2O_2, added periodically to prevent pitting	
pH,	2.0 ± 0.2

2. Temperature, 140 F

B. Current density, 40 amp/sq ft

C. Plate thickness, 1.0 - 2.0 mils

VII Rinse and Dry

VIII Prebake

A. Temperature, 400 F

B. Time, 2 to 4 hours

IX Thermal-Diffusion Bonding

A. Temperature, 1300 F

B. Time, 10 to 45 minutes

C. Atmosphere, air or argon

D. Quench, water, air, or argon

In this procedure, the nickel-plate thickness is specified as 1.0 to 2.0 mils (0.001 to 0.002 inch). Other metal or more nickel should be plated after diffusion bonding and activation of the first nickel.

XI Nickel Activation

A. Solution specifications

1. Composition

H_3PO_4, 150 g/l
HCl, 9 g/l

2. Temperature, 80 ± 10 F

3. Current density, 100 amp/sq ft

4. Polarity, anodic

XII Rinse

XIII Plate

Nickel or other metals

The composition range of the solution (IV) for etching zirconium has been extended. The ratio of ammonium fluoride to hydrofluoric acid influences the as-plated adhesion. Zirconium etched in solutions with NH_4F/HF molar ratios of 1.2 to 4.1 and nickel plated showed the best as-plated adhesion and the best diffusion bonding. Zirconium etched in solutions with NH_4F/HF molar ratios of less than 1.0 or greater than 16.6 and nickel plated showed inferior as-plated adhesion and inconsistent diffusion bonding.

Electrodeposition of nickel (VI) on etched zirconium from a low-pH (2.0) Watts bath (wetting agent free) is recommended. Nickel plates from this low-pH bath are less subject to pitting than those from the high-pH (4.0) bath. Organic addition agents to reduce pitting are not recommended for the initial 0.5 mil of plate, because they are included in the deposit, and the diffusion alloy results in a weaker alloy bond. Periodic addition of hydrogen peroxide to the plating bath is used to prevent pitting.

The suggested thickness of electroplated nickel for diffusion bonding to zirconium or zirconium alloy is one to two mils. About one-half mil of the nickel alloys with the zirconium, leaving one-half or more of virtually unalloyed nickel for subsequent operations. If the nickel plate is too thick, separation of the as-plated bond occurs during heat treatment, because of the difference in thermal expansions of nickel and zirconium.

For As-Plated Bonding

Further attempts to improve the as-plated adhesion of electroplated metal on zirconium so as to approach the diffusion bond strength (50, 000 psi) were unsuccessful.

Earlier attempts to produce satisfactory as-plated adhesion, using an immersion or replacement metal film (zinc, iron, nickel, or copper) on the zirconium prior to electroplating, were not very encouraging. However, the similarity of the atomic distances in zirconium and indium suggested the possible formation of a chemical bond between the two metals if an indium film continues the crystal structure of the zirconium. Indium was replacement deposited onto zirconium by immersion in a solution of indium fluoborate. Nickel electroplated on indium-coated zirconium showed as-plated adhesion comparable to that of nickel electroplated on etched zirconium (about 6, 000 psi, the strength of soft solder). Since the strength of indium is low, high-strength as-plated adhesion could not be expected; however, satisfactory diffusion bonding at temperatures below 1300 F appears promising. This phase will be studied further.

Tin, lead-tin solder, and silver solder can be applied adherently to zinc-coated zirconium surfaces. The zinc coating is applied by immersing zirconium in molten (440-450 C) zinc chloride salt. The as-plated adhesion of nickel on hot-dip tin- or solder-coated zirconium was equal to the strength of tin (2, 000 psi) or solder (6, 000 psi).

Aluminum was plated on zirconium from nonaqueous organic baths(3). On unetched zirconium, the aluminum was peeled easily. On etched zirconium, the adhesion of aluminum was about the same as that of nickel on etched zirconium. Diffusion bonding at a temperature below 1300 F was indicated.

SUMMARY OF EXPERIMENTAL RESULTS

As-Plated Adhesion

The best as-plated adhesion of electroplated metals to zirconium found in this work has been about 6, 000 psi (the strength of soft solder), as indicated by moduli of rupture. Such as-plated adhesion was observed for nickel, iron, and aluminum electroplated onto etched zirconium or zirconium-tin-alloy surfaces.

(3) Brenner and Couch, "Electroplating of Aluminum", J. Electrochem. Soc., June or July, 1952.

Etching of Zirconium for Direct Plating

Nickel, iron, and aluminum are electroplated on zirconium or zirconium-tin alloy (2.5 per cent tin in crystal-bar zirconium) after etching in solutions containing ammonium fluoride and hydrofluoric acid. The as-plated adhesion and subsequent diffusion bonding are dependent on the ratio of the ammonium fluoride and the hydrofluoric acid in the etching solution. The relationship is shown in Table 1.

TABLE 1. THE EFFECTS OF CONCENTRATION AND MOLAR RATIO OF AMMONIUM FLUORIDE AND HYDROFLUORIC ACID IN THE ETCHING SOLUTION FOR ZIRCONIUM ON THE AS-PLATED ADHESION OF ELECTROPLATED NICKEL

NH_4F, mol/liter	HF, mol/liter	NH_4F/HF molar ratio	As-Plated Adhesion, psi
0.00	0.50	0	<1000
0.44 to 0.88	0.44 to 0.88	1.0	<1000
0.49 to 0.98	0.40 to 0.80	1.2	>6000
0.66 to 1.32	0.22 to 0.44	3.0	>6000
0.83	0.05	16.6	<1000
1.67	0.09	18.8	<1000

Nickel Plating on Zirconium

Three nickel-plating baths were used in this study:

	Bath A	Bath B	Bath C
$NiSO_4 \cdot 7H_2O$	330 g/l	240 g/l	300 g/l
$NiCl_2 \cdot 6H_2O$	46 g/l	45 g/l	50 g/l
H_3BO_3	37 g/l	30 g/l	30 g/l
H_2O_2	Added periodically to prevent pitting	----	----
NaCOOH	----	----	15 g/l
XXXD(4)	----	----	20 cc/l
pH	2.0	4.0 to 4.5	4.0
Temperature	140 F	110 F	140 F
Current density	40 amp/sq ft	40 amp/sq ft	40 amp/sq ft

(4) Proprietary wetting-agent solution marketed by Harshaw Chemical Company, Cleveland, Ohio.

No difference in the as-plated adhesion could be attributed to the type of plating bath.

Pitting of the nickel from Baths A and B is prevented by empirical, periodic additions of hydrogen peroxide. However, nickel plated from Bath A was less subject to pitting and therefore is preferred. Pitting of the nickel was avoided with a wetting agent in Bath C. However, the wetting agent in Bath C affects the diffusion alloying, as discussed later.

Aluminum Plating on Zirconium

A conjectured reason for the inability to improve the as-plated adhesion is the formation of zirconium hydride on the surface of the metal. This zirconium hydride would be a weak, interfacial layer, and its decomposition, liberating hydrogen, would accentuate the weakness.

In an attempt to avoid this hydride formation, aluminum was electrodeposited on etched and unetched zirconium samples in a nonaqueous organic bath(3) of ethyl ether, lithium hydride, and aluminum chloride. The as-plated adhesion of the aluminum on etched zirconium was comparable to that of nickel electrodeposited from aqueous baths on unetched zirconium. As with nickel, etching of the zirconium improved the as-plated adhesion of the aluminum.

Chromium Plating on Zirconium

Chromium can be plated over nickel diffusion bonded to zirconium. Chromium plated directly on etched zirconium exfoliates because of the as-deposited internal stress of the electrodeposited chromium from the customary, chromic acid plating bath.

Several chromium-plating baths containing fluoride or fluoride complexes were formulated in an attempt to provide a bath for simultaneous activation and chromium plating of a zirconium surface. These attempts were failures, in that even small amounts of fluoride in the baths resulted in attack on the zirconium surface and prevented satisfactory deposition of chromium.

(3) Bremer, et al., loc. cit.

Diffusion Bonding of Electroplated Metals on Zirconium

Nickel

Since nickel diffusion bonded to zirconium can be a basis for subsequent electroplating with more nickel or with other metals, most of this work was centered on nickel diffusion bonded to zirconium and zirconium-tin alloy.

The as-plated bond (about 6000 psi) of nickel on zirconium, after prebaking (2 hours at 400 F) and heat treating (10 to 45 minutes at 1300 F), is increased to 40,000 to 50,000 psi. Nickel plated from wetting-agent-free baths and heat treated gave the best alloy bonds (50,000 psi, as indicated by moduli of rupture). About 0.5 mil of the nickel alloys with the zirconium. Nickel plated from baths containing wetting agents (Bath C, previous section) directly on etched zirconium [or plated over thin (< 0.5 mil) nickel (wetting agent free) on zirconium] and heat treated gave weaker alloy bonds (40,000 psi).

Aluminum

Heat treatment of electroplated aluminum on zirconium in a gas burner flame produced mostly blistering. An area or two of good bonding also occurred. The details of diffusion bonding electroplated aluminum or zirconium were not investigated.

Replacement Metal Coatings on Zirconium

Indium

Most acid fluoride solutions of metal salts will replacement deposit a film of the metal onto the zirconium. Generally, most of these metal deposits show only an apparent adhesion, in that they can be peeled easily if plated over with sufficient metal. Such films are comparable to copper film applied to steel by immersion in acid copper sulfate solutions.

Indium films on zirconium, applied by immersion in a commercial indium fluoborate solution,[5] show encouraging as-deposited adhesion. Nickel electroplated over this indium film on zirconium showed good

(5) Marketed by General Chemical Company, Cleveland, Ohio.

as-plated adhesion (about 6,000 psi). Slight heating of nickel-plated, indium-coated zirconium in a gas burner flame improved the as-plated bond, presumably by low-temperature diffusion alloying.

Indium and zirconium both have coordination numbers 12, and have similar atomic arrangement and atomic distances. Zirconium is close-packed hexagonal, with the closest atomic spacing of 3.16 A, whereas indium is face-centered tetragonal with the closest atomic spacing of 3.24 A on hexagonal faces. These similarities should aid continued growth of the zirconium crystals into the indium film and thereby provide maximum adhesion.

Zinc

Zinc was applied to zirconium surfaces by immersion in molten (450 C) zinc chloride. Presumably the zirconium oxide formed volatile zirconium chloride and the zinc deposited on the zirconium surface. Tin, soft solder (50 Pb-50Sn), and silver solder (mp 1080 F) were applied to this zinc-coated zirconium surface by conventional means. Nickel plated on tin-coated zirconium showed a bond of 2000 psi (the strength of tin) and nickel plated on solder-coated zirconium showed a bond of 6000 psi (the strength of solder), as indicated by moduli of rupture. The tin, soft solder, and silver solder apparently diffused with the zinc coating on the zirconium, forming strong solder bonds.

Copper or nickel electrodeposited directly on the zinc-coated zirconium surfaces, using conventional methods for plating on zinc, was weakly bonded. The zinc coating adhered to both the electroplated metal and the zirconium, but bond failure appeared to occur within a brittle zinc-zirconium-alloy layer. Attempts to avoid such failure by heat treating the zinc-coated zirconium were not successful.

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